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Research review paper

Natural antifouling compounds: Effectiveness in preventing invertebrate settlement and adhesion

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ABSTRACT

Biofouling represents a major economic issue regarding maritime industries and also raise important environmental concern. International legislation is restricting the use of biocidal-based antifouling (AF) coatings, and increasing efforts have been applied in the search for environmentally friendly AF agents. A wide diversity of natural AF compounds has been described for their ability to inhibit the settlement of macrofouling species. However poor information on the specific AF targets was available before the application of different molecular approaches both on invertebrate settlement strategies and bioadhesive characterization and also on the mechanistic effects of natural AF compounds. This review focuses on the relevant information about the main invertebrate macrofouler species settlement and bioadhesive mechanisms, which might help in the understanding of the reported effects, attributed to effective and non-toxic natural AF compounds towards this macrofouling species. It also aims to contribute to the elucidation of promising biotechnological strategies in the development of natural effective environmentally friendly AF paints.

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1. Introduction

The establishment of new benthic biological communities in aquatic environments either in living or non-living substrata (biofouling) generally involves a sequence of succession started by the accumulation of a biochemical proteinaceous conditioning followed by bacteria, unicellular and multicellular eukaryote colonization (Wahl, 1989). The initial step of microbial biofilm formation (microfouling) is known to regulate the subsequent colonization of macroalgal spores and invertebrate larvae (macrofouling) (Pawlik, 1992). Biofilm properties, including physical characteristics, biotic composition and produced chemical signals have been reported to act as either a stimulatory or inhibitory stimulus for the settlement of a particular macrofouling community

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(Dobretsov et al., 2006; Hellio et al., 2005; Pawlik, 1992; Qian et al., 2007). Nature provides good models of antifouling (AF) by a combination of this chemical cues, and also physical properties including surface roughness and fluid hydrodynamics. Mussels, crabs, and sharks, among others, possess exterior surfaces that are able to inhibit epibiosis and biofouling (Hadfield and Paul, 2001; Magin et al., 2010). In addition, some species of macroalgae (Daoud et al., 2011; Eashwar et al., 2008; Hellio et al., 2002), sponges (Engel and Pawlik, 2000; Hellio et al., 2005; Sjogren et al., 2008), soft corals (Nagabhushanam et al., 1995; Slattery et al., 1995), and ascidians (Cima and Ballarin, 2012; Menin et al., 2008; Teo and Ryland, 1995) have also the ability to prevent epibiosis, by their own chemical cues, which may range from small-molecule secondary metabolites to high-molecular weight extracellular polymers (Fusetani, 2011; Hadfield, 2011). Along with natural surfaces, all submerged artificial structures such as ships, pipelines, oil platforms, bridge pillars, and fishing devices subjected to biofouling suffer adverse impacts. Particularly on ships, higher fuel consumption and decreased speed and range are attributed to increased frictional drag (Schultz, 2007; Schultz et al., 2011; Yebra et al., 2004), and thus biofouling control is mandatory for maritime industries. The majority of antifouling paints currently in use are based on biocidal agents that induce general toxic responses in the marine environment associated with heavy metal toxicity and antibiotic toxicity, among others. Considering this, a need to develop alternative non-toxic and environmentally friendly AF agents arise in line with the EU Biocidal Product Regulation (EU) 528/2012, which led to increasing investigation on the field of natural AF compounds. A wide range of natural products have been screened for their potential to substitute the efficient but extremely toxic tributyltin (TBT), now banned in 27 countries (IMO, 2008). Some alternative booster biocides have also been introduced and believed to be less harmful for the environment, however significant environmental risks were also identified (Konstantinou and Albanis, 2004; Thomas and Brooks, 2010). A wide range of natural AF compounds from diverse source species has been identified lately by their ability to inhibit the settlement of macrofouling species (Fusetani, 2011). Recent investigations on this topic permit us to recognize that microorganisms in particular are promising potential sources of non-toxic or less-toxic AF compounds, as they produce a wide-range of potentially bioactive metabolites and also have the advantage of being easy to culture and to produce in large scale in short periods of time, easily ensuring product supply renovation for commercialization (Burgess et al., 2003; Dahms et al., 2006; Dobretsov et al., 2006, 2013a; Gademann, 2007; Qian et al., 2007; Tan et al., 2010).

However, AF compounds identification is often based on a single and general endpoint/mechanism of action, showing a narrow spectrum performance towards the biofouling community (different species and different life stages), compromising their effectiveness and their incorporation in AF paintings. Regarding the variety of adhesion mechanisms and settlement strategies among biofouling organisms, several general modes of action of natural products are described including repellants, toxins, surface energy modifiers, nervous pathway interference (both anesthetics and neurotransmitters) and inhibitors of growth, attachment, adhesion or metamorphosis (Clare, 1996; Rittschof, 2000). However, the challenge remains in the identification of molecular mechanisms underlying the bioadhesion of a majority of biofouling organisms and the potential common effects of natural AF compounds. Increasing efforts and up-to-date techniques have been lately applied on this subject to identify and characterize different settlement and metamorphic transition processes as well as characterize bioadhesives (Chandramouli et al., 2012a,b; Gantayet et al., 2013; Thiyagarajan et al., 2009; Williams and Degnan, 2009; Zhang et al., 2010b). Also, the effects and modes of action of a range of AF natural compounds have been tested and identified against different biofouling species (Fusetani, 2011; Qian et al., 2013). Thus, there is a need to find common denominators mediating effectiveness in attachment that could be controlled by a specific combination of mode(s) of action.

In this context, this review highlights the recently produced knowledge on identification and characterization of the main invertebrate macrofouler species settlement strategies and bioadhesive mechanisms, and also on the reported effects and modes of action described for effective and non-toxic natural AF compounds isolated from a variety of organisms towards invertebrate macrofouling species. This review aims to contribute to the identification of promise strategies to select broad-range natural AF compounds suitable for the development of effective environmentally friendly AF paints.

2. Diversity of invertebrate macrofouling adhesive strategies

2.1. Innate settling criteria

Despite biofouling adverse effects start with the formation of biofilms, the most disturbing component of this event is the colonization of hard foulers that constitute the macrofouling. Bryozoans, molluscs, barnacles, polychaetes and tunicates constitute the most dominant groups, whose larval stages are induced to settle on selected underwater surfaces. Invertebrate larvae are able to actively select by prospection the most attractive place to adhere regarding many aspects such as surface topology, wettability, chemistry, light exposure, streaming conditions, and substrate color, among others (Aldred et al., 2006; Carl et al., 2012; Di Fino et al., 2014; Dobretsov et al., 2013b). This selection is specific on the species and is based on a combination of surface characteristics, also including biological cues (Kristensen et al., 2008). These biological settlement signals might involve both conspecific cues and extracellular polymeric substances (EPS) provided by bacteria. The constitution of previously formed biofilms will attract specific macrofouling species and repel others that in the same way might be attracted by other biofilm properties or even by biofilm-free surfaces (Hadfield, 2011; Qian et al., 2007; Wahl et al., 2012). Such responses are well-documented in the main macrofouling species such as the bryozoan *Bugula neritina* (Dahms et al., 2004; Dobretsov and Qian, 2006), the polychaete *Hydroides elegans* (Chung et al., 2010; Harder et al., 2002; Lau et al., 2003; Shikuma et al., 2014), the mussels from the genus *Mytilus* (Bao et al., 2007; Carl et al., 2012; Satuito et al., 1995; Toupoint et al., 2012; Yang et al., 2008) and the barnacle *Balanus amphitrite* (Harder et al., 2001; Zardus et al., 2008). In this context, quorum sensing (QS) signals, responsible for biofilm formation, propagation and maturation in a density dependent cell-to-cell communication and gene regulation process, have also been found to have a role in the regulation of settlement of macrofoulers (Dobretsov et al., 2009, 2011). Evidences show that the inhibition/induction of settlement is dependent on the nature of the bacterial biofilms regarding the production/absence of proteolytic enzymes (Dobretsov et al., 2007).

Conspecific cues also play a crucial role as settlement inducers. Conspecific density and gregarious preferences are common characteristics among macrofouling species including mussels (Kobak, 2001; Ompi, 2011; Vooys, 2003), polychaetes (Qian, 1999) and barnacles (Aldred and Clare, 2008), however, the nature and potential of the responsible pheromones are underexplored in many of these species, except for barnacles which have been the focus of extensive investigation. One of the described biogenic cues responsible for the gregarious settlement and species recognition during settlement in barnacles is a contact pheromone known as the settlement-inducing protein complex (SIPC) (Dreanno et al., 2006a, 2007; Elbourne and Clare, 2010). SIPC-like proteins are cuticular glycoproteins of high molecular mass (76–98 kDa), with lentil lectin (LCA)-binding sugar chains showing sequence similarities to alpha2-macroglobulin (A2M) protein family (Dreanno et al., 2006b; Matsumura et al., 1998). Based on identification and characterization of settlement-inducing proteins with similar molecular weight than SIPC, recent investigations considered SIPC as a component of arthropodin protein complex (APC), the first peptide signal molecule attributed to promote gregarious settlement (Khandeparker and Anil, 2011; Knight-Jones, 1953). Other peptides